

# **A Demonstration of SILVER II<sup>®</sup> for the Decontamination and Destruction of Organics in Transuranic Wastes**

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## **1. Introduction**

SILVER II<sup>™</sup> is AEA Technology's patented process for the mineralization of a wide range of organic substrates. It has been developed over a number of years from laboratory to plant scale, culminating in the Assembled Chemical Weapons Destruction Program conducted on behalf of the US Army over the summers of 2000 and 2001. The 12kW plant designed and constructed for the Army was approximately 40' x 20' x 30' high which gives an illustration of the current maturity of this technology.

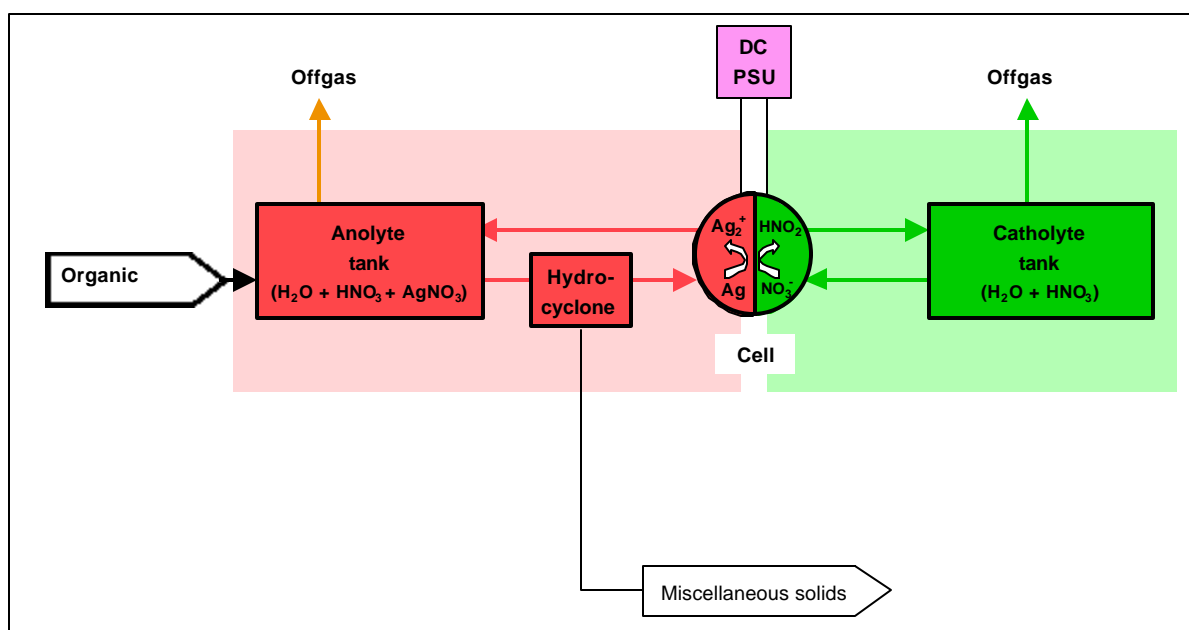
Initial work in the 1980's was directed towards the treatment of radioactive contaminated organic wastes, comprised of solvents, PUREX extractants, ion-exchange resins, cellulosic tissues and polymeric materials. The organic components were converted to CO<sub>2</sub> and water, which could be safely discharged into the environment, leaving a minimal volume of radioactive residues for immobilization prior to storage and then disposal.

Chemical Weapons are a second category of hazardous materials requiring treatment as part of their management strategy. While the current reference route for disposal is incineration, a program was initiated by the US Army, in response to public concerns in the United States, to investigate alternative treatment methods, including SILVER II<sup>™</sup>. While initial work was conducted with small pilot-scale equipment, subsequent demonstrations were based on full-scale commercial electrochemical cells, such as those used in the Chlor-Alkali industry. The SILVER II approach is therefore based on well-proven, off-the-shelf technology and components.

At the heart of the SILVER II process is the chemical oxidation of organic molecules by the Ag[II] ion. This is one of the most oxidizing species that can be generated at an anode in an electrochemical cell in aqueous solution (see Figure 1). Radical species initiated by Ag[II] attack the organic substrate, progressively converting it in a series of steps irreversibly to CO<sub>2</sub>, water and residual salts from hetero-atoms (including halides, sulfur, nitrogen and phosphorus). During the oxidation step, Ag[II] is reduced back to Ag[I]. This is then regenerated to Ag[II] again at the electrochemical anode. This "catalytic" use of silver makes this a Mediated Electrochemical Oxidation (MEO) Process.

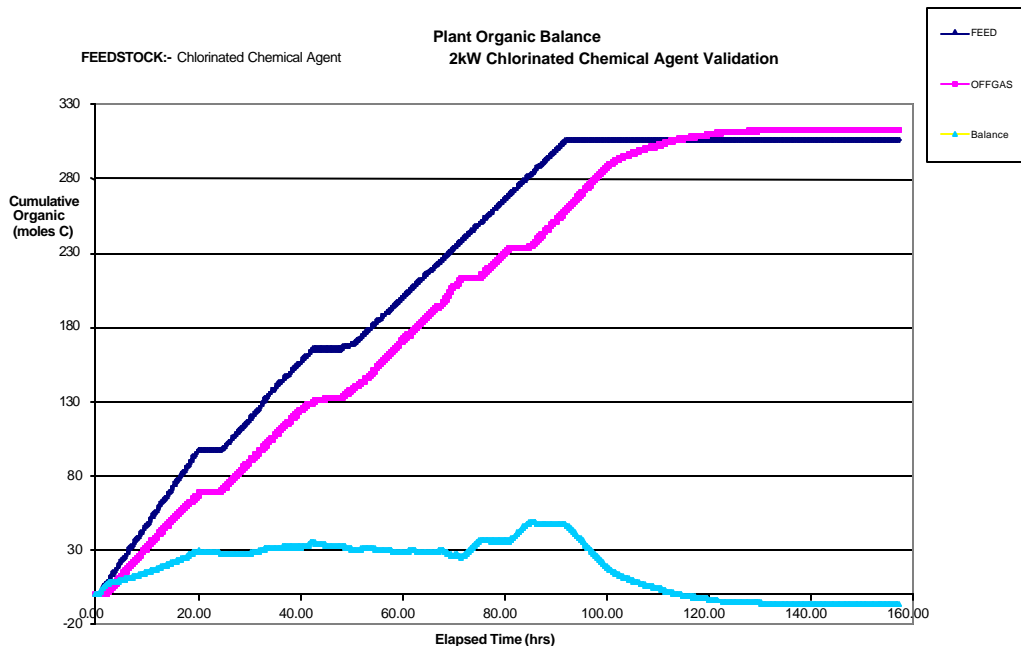
The organic species do not have to be water-soluble to be successfully treated by SILVER II™, as has been shown by the successful treatment of solvents, oils, ion-exchange resins, tissues and other organics.

The series of reaction steps between Ag[II] and the organic intermediates is like a pipeline in the steady-state, where the relative concentrations of each intermediate is inversely proportional to the reaction rate with Ag[II]. Ag[II] can also react slowly with water, giving O<sub>2</sub> as a parasitic product. In order to minimize this loss route, the concentration of organics should be high (2-10g/l C), with high mass transfer rates to optimize the coupling of the generation and reaction steps by maximizing interfacial area between immiscible phases. The optimal temperature for efficient usage of electrical energy is ~90°C where the reactions with the organic substrates are rapid. CO<sub>2</sub> is rejected from the acidic electrolyte into the gas stream, which is scrubbed prior to discharge to atmosphere.



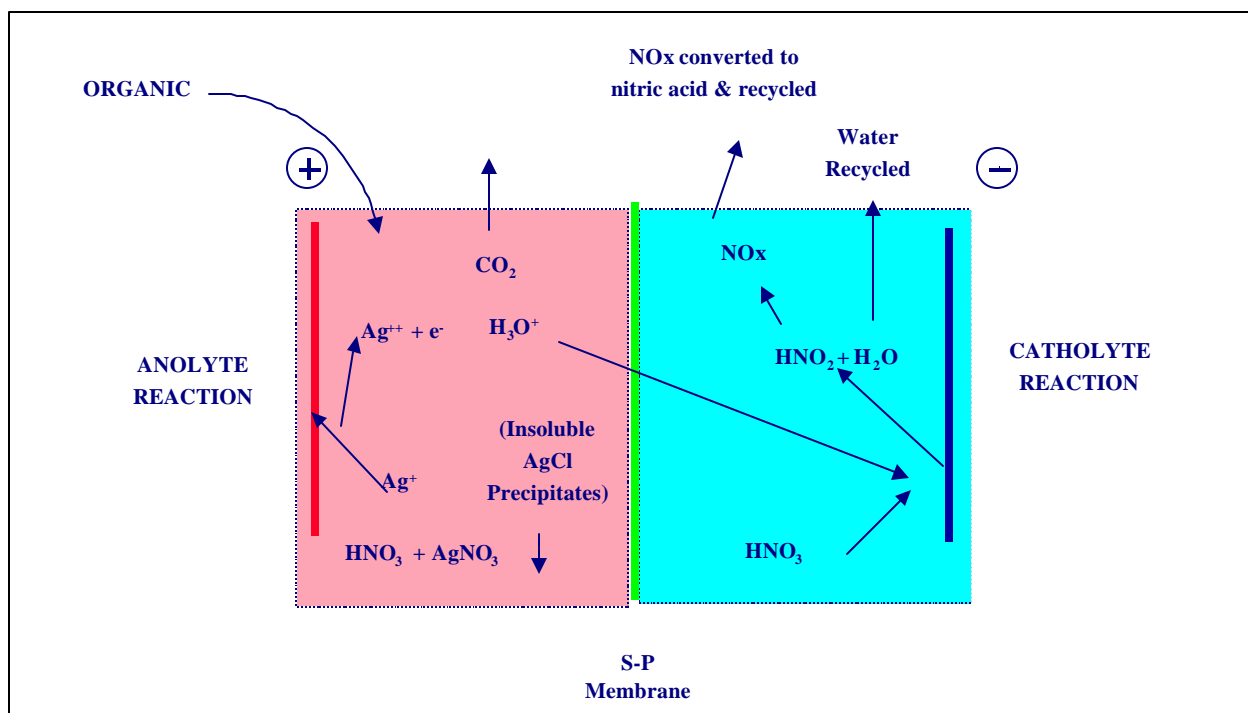
**Figure 1 Schematic layout of the core SILVER II™ process**

The heart of the system is shown in **Figure 1**. The Ag[II] is generated *in-situ* electrolytically, at the anodes of commercially available electrolytic cells. It is the linkage between these two steps that provides the benefits of the process, in that the reaction rate can be controlled by the applied current. The rate of organic feed is matched to the rate of destruction defined by the electrolytic regeneration process as illustrated in Figure 2.



**Figure 2 Organic balance during the treatment of Chlorinated Chemical Agent in the 2kW ACWA plant**

In the case of chlorine-containing feeds, the chloride content will precipitate as silver chloride. This is prevented from entering the cell by solid/liquid separation in a hydrocyclone. The recovered material can be treated to recover the silver, which can be returned to the electrolyte for re-use.

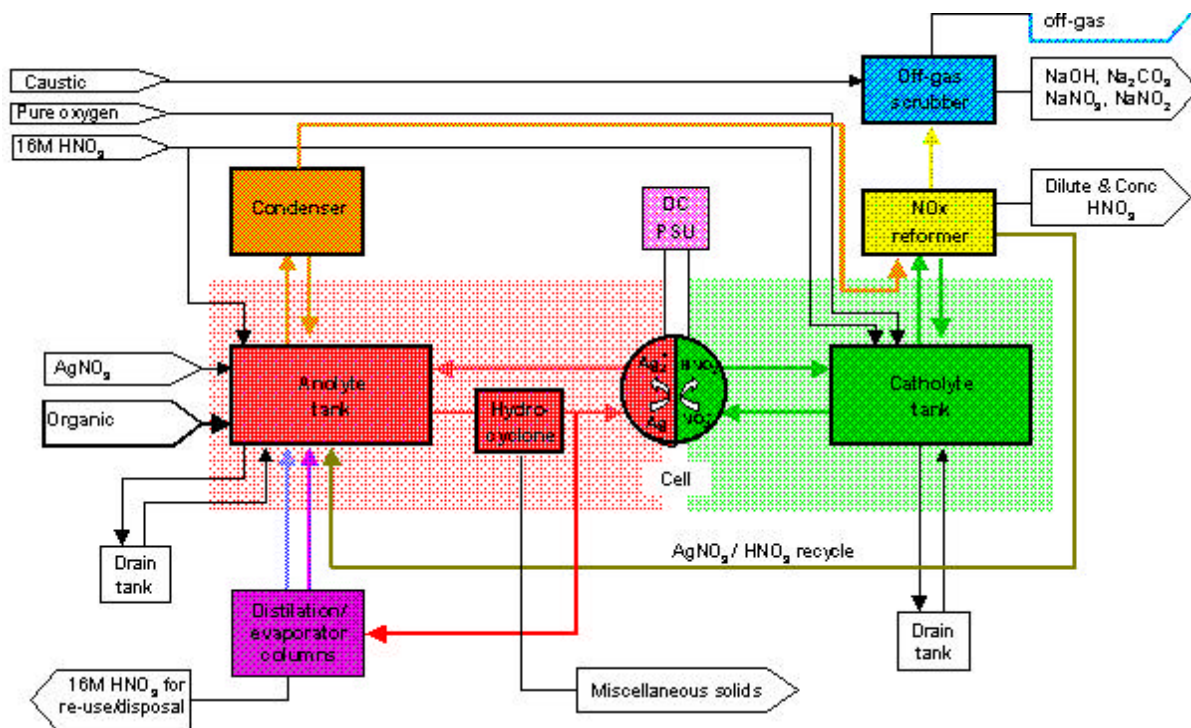


**Figure 3 The SILVER II™ cell reaction**

The matching reaction at the cathode of the electrochemical cell is the reduction of nitric acid to nitrous acid, which results in the evolution of NO and NO<sub>2</sub>. Oxygen/air is drawn through the plant so that the NO<sub>x</sub> can be reformed back into nitric acid through simple chemical reaction. This stream can then be fractionally distilled to recover concentrated nitric acid for internal recycling within the process, and water (with minimal nitric contamination) for discharge resulting from the hydrogen content of the feed. After this stage, the off-gas is finally scrubbed prior to venting to remove any residual traces of NO<sub>x</sub>. The overall process schematic is shown in Figure 4.

As can be seen, internal recycle of water, acid, silver are engineered to minimize environmental discharges. These are restricted to CO<sub>2</sub> (from the C content of the feed), excess H<sub>2</sub>O (from the H content of the feed) and acids (derived from the hetero atom content of the feed), which can be lime neutralized prior to discharge.

As the process uses commercially available “off-the-shelf” components, and is based on an “industry-standard” electrochemical cell for commodity chemical manufacture, this technology is considered mature. The operation of two integrated plants was demonstrated during 2000 as part of the US Army ACWA program for a total of more than 3500 hours operation (equivalent to 25000 man hours or approximately 2 years of operation at 8 hours per day).



**Figure 4: Overall process schematic**

## **2. Prior uses of technology**

Early use of SILVER II<sup>TM</sup> was by AEA in the United Kingdom (UK) in the 1980's for the dissolution of insolubles from fast reactor fuel reprocessing as well as treatment of radioactive contaminated tissues and swabs.

During this early work it was identified that cellulosic materials are completely oxidized to CO<sub>2</sub>, minor amounts of CO and water by Ag(II). Trials with radioactive contaminated tissues on a small scale showed that associated radioactive element, either in the form of the nitrate or radioactive oxide, was completely dissolved. Dissolution trials on the solids obtained from the caustic washing of combustible alpha waste (Polyvinyl Chloride (PVC), Polyethylene (PE), tissues containing 0.1-1% of the radioactive element originating from thermal reactor irradiation) demonstrated the destruction of the cellulosic component.

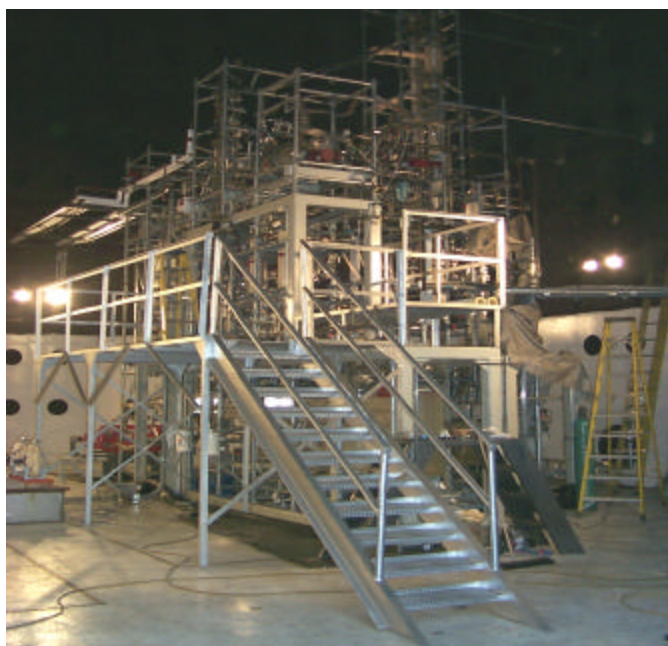
It was also demonstrated that polymeric wastes were attacked only very slowly under the optimum conditions for the radioactive element dissolution (20-40°C). Leaching trials on finely ground radioactive containing slag (siliceous, containing Al and some other metals) showed little or no radioactive element dissolution due to a similar incorporation of the radioactive element into an insoluble matrix.

There is some attack on comminuted PE and PVC under organic oxidation conditions (60-90°C), but the rate is such that the overall electrochemical efficiency is too low for practical bulk destruction of plastics without some pre-treatment. Only PE has been the subject of limited trials in this respect. High Density Polyethylene (HDPE) pipette tips were digested at reflux in 16M HNO<sub>3</sub> to give a homogeneous solution. This was then diluted, AgNO<sub>3</sub> added and the solution subjected to MEO in a lab cell, when the solubilized organics were completely mineralized. The practicalities of this approach have not been the subject of detailed assessment or larger-scale

trials, nor have trials with PVC been carried out. It is anticipated that nitric acid pre-treatment of PVC would probably produce HCl, which could give rise to some corrosion issues. However, it is believed that once the components are solubilized there is a good chance that the residual organics are easily oxidizable. As a result, the use of SILVER II™ with the polymeric components of the DOE waste would be more in the role of decontaminant rather than complete mineralization.

More recently, SILVER II™ evaluation work has been carried out in the UK on the mineralization of oils, combustible waste and radioactive oxide dissolution for commercial customers.

SILVER II™ has been demonstrated with full-scale commercial electrolysis cells for the processing of Tributyl Phosphate (TBP), as well as part of the US Army ACWA program on destruction of Chemical Warfare Agents and Energetics. The former was carried out with a single cell, while the latter was carried out in a unit of three cells operated in parallel – both as fully integrated plants. Treatment of TBP/Odorless Kerosene (OK) was recently conducted on this plant as part of an EM-50 funded effort before the most recent phase of the ACWA program.



**Figure 5 12kW SILVER II plant used for the ACWA demonstration**

In summary, SILVER II™ is a well proven, mature technology which will completely destroy organics present in typical DOE waste streams and which will decontaminate the polymeric constituents enabling them to be discharged as lower level waste, thereby saving DOE significant amounts of money in disposal and handling costs.

### 3. Benefits of SILVER II™

In summary, the benefits of SILVER II™ are as follows;

- It operates at ambient pressure and low temperature (20 – 90°C). At the lower end of this range, radioactive oxide dissolution is rapid, while organics mineralization is slow. As the temperature is raised, the rate of organics oxidation increases. As a result, none of the toxic or carcinogenic discharges associated with incineration (including dioxins, furans, polyaromatic hydrocarbons) are formed.
- The process has a high degree of public acceptability and regulatory ‘permissibility’ as a result of its inherent safety.
- It is easily controllable since it can be stopped, simply by switching off the electricity to the system. This contributes to achieving ALARA goals in equipment construction and operation.
- The plant is self-decontaminating, due to the fact that Silver II™ dissolves the radioactive oxide contaminant. This can then easily be rinsed out with nitric acid.
- It is a genuine waste volume reduction technology i.e. it does not generate larger volumes of less toxic waste.
- It is non-discriminatory (i.e. it will attack any organic). It is well proven over 16 years of development and operation
- It has minimal off-gas produced and this enables hold-up and analysis before discharge to the atmosphere.
- It has a very large degree of recycle of chemicals such as silver and nitric acid as detailed above which minimizes the environmental impact of the entire system.
- It operates in a continuous mode and therefore the process has a very low steady-state inventory of chemicals.
- It performs a very effective decontamination on those materials that it is unable to destroy completely. For example, while Silver II™ can mineralize cellulose, rubbers and ion-exchange resins, polymeric sheets react more slowly due to their lower specific surface area. Chlorine containing polymers (e.g. PVC) are even more resistant to attack than polypropylene or polyethylene. However, so long as the Silver II™ solution can gain access to the radioactive oxide contamination sites, it will dissolve the radioactive element readily. As a result, residual plastic, glass and ceramic components are expected to be sufficiently decontaminated to meet low-level alpha packaging and shipping requirements. This will also reduce radiolytic hydrogen generation due to the significant reduction in the radiation field. The radioactive waste will contain <<5% organics, to meet TRUPACT packaging and shipping requirements. Both of these materials can be cemented to provide waste-forms able to meet the WIPP acceptance criteria. The following table identifies the type of treatment SILVER II™ will perform given the material type.

Material	Mineralization	Decontamination
PVC		✓
Nylon	✓	
Plexiglas		✓
Lexan		✓

Nitrile gloves	✓	
Polyethylene		✓
Polystyrene	✓	
Polypropylene		✓
Cellulose	✓	
Leather	✓	
Oil	✓	
Rubber	✓	
Paint	✓	
Chemical reagents	✓	
Solvents	✓	
Carbon steel	✓	
Stainless steel		✓
Tin	✓	
Copper	✓	
Lead	✓	
Cadmium	✓	
Platinum		✓
Ceramics		✓
Resins	✓	

- The plant is simple and safe to operate as has been demonstrated by the training and operation of the ACWA SILVER II™ plants by US Army personnel during the 2000 and 2001 demonstration programs at Aberdeen Proving Grounds, Maryland.
- The Silver II™ plant can be constructed of materials able to withstand high radiation doses – including stainless steel for the catholyte circuit and titanium for the anolyte circuit. AEA Technology has demonstrated an electrolytic cell with a ceramic ultraporous separator for use with active solutions, as an alternative to the more usual Nafion™ membrane. Insulating components required within the cell can be fabricated from polyvinylidene (PVDF), which is substantially more radiation tolerant than the more commonly used polyethylene tetrafluoroethylene (PTFE). Inorganic fillers in the Viton seals confer a higher radiation tolerance as well as high resistance to chemical attack.

#### 4. US DOE Supported Programs

##### 4.1 Destruction of TBP/OK

The US Department of Energy has expressed an urgent need to identify technologies that are capable of destroying radioactive mixed waste streams. To meet the US DOE requirements, the technologies must be alternatives to incineration. This program utilized the Silver II process to destroy the organic components of a simulant waste stream that is commonly generated during reprocessing activities. The demonstration of the SILVER II system was conducted in a pilot plant currently being used by the US Army for the destruction of chemical agents at the Aberdeen Proving Ground.

The major benefits of AEA Technology's SILVERII™ technology for this application are:



- It can achieve an activity volume reduction of 94% for a 20% tributylphosphate/odorless kerosene mixture<sup>1</sup> with a resulting reduction in waste storage costs. Significantly higher volume reduction factors can be achieved by separating the active components from the phosphate residue.
- The active waste can be limited to a solid product that is amenable to disposal and does not contain flammable hydrocarbons or toxic products.
- This is a low temperature process that does not produce dioxins or polyaromatic hydrocarbons (PAHs).
- It has a positive public perception when compared to a baseline process such as incineration.

Utilizing a pre-existing SILVERII facility had a number of benefits to DOE specifically;

- There was no associated equipment capital expenditure.
- There was no associated facilities capital expenditure.
- The operation was carried out at plant scale, thus minimizing any risks associated with scale-up.
- The project team was already in place, thus minimizing training costs.

The deliverables from this program will be comprised of:

- The successful completion of a plant-scale simulant demonstration of the process.
- Demonstration of the impurities handling/recycle system during this period of operation in order to provide an indication of the potential for further volume reduction.
- A report detailing Destruction Removal Efficiency, throughput, energy utilization, effluents, chemical utilization, price/implementation.

#### **4.2 Destruction and Decontamination of Organics in Transuranic Wastes**

The United States Department of Energy has large quantities of 55-gallon drums of radioactive contaminated waste in interim storage. These may not be shipped to WIPP in TRUPACT-II containers due to the high rate of hydrogen production resulting from the radiolysis of the organic content of the drums. In order to circumvent this problem, the radioactive element needs to be separated from the organics – either by mineralization of the latter or by decontamination that can perform a chemical separation

Under contract DE-AC26-01NT41201 AEA Technology is offering its proven, patented SILVER II™ technology for evaluation against this application, operating as a partial mineralization combined with decontamination. The Phase I program will be carried out by AEA Technology in the UK to establish proof of principle at laboratory scale on surrogate waste streams. This plant will then be shipped to the DOE for installation in a glove-box facility for hot trials with radioactive contaminated waste. After completion of evaluation trials, a design of >1/5 scale demonstrations will be presented as part of the final report.

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<sup>1</sup> Assumes that the phosphate is converted to calcium phosphate (with bound activity), organic components to carbon dioxide and water, and complete chemical recycle of process liquors.